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**Hygrophotographic Studies on the Permeability
of Packaging Materials to water and Moisture**

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Paris XV

Contract Number N° DA-91-591-EUC-2152

Final Technical Report FTR N° 3, 31 January 1963

**Covering the period February 1st 1962 to January
31, 1963.**

**"The research reported in this document has been made
possible through the support and sponsorship of the
U.S. Department of Army through its European Research
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Paris, XV

To: European Research Office (9851 DU)
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FINAL TECHNICAL REPORT

Subject

Hygrophotographic Studies on the Permeability
of Packaging Materials to Water and Moisture

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-Page Two-

TABLE

Summary of the Report (Abstract)	Page 3
Final General Report	6
Annex	17

ABSTRACT

In our two previous final reports we exposed the results which we had obtained from the study of the permeability of a great number of plastic films in that which concerns water and humidity in a limited temperature of 25 to 65° C.

While the tests on permeability at the normal temperature of 25° were carried out in liquid water, the tests at elevated temperatures took place only in an atmosphere saturated by steam. We have indeed admitted, perhaps without valid reason, that at the contact of hot water, the properties of plastic materials could have undergone profound modifications; the results obtained under these conditions could be without any relation to the normal properties of the films studied.

However, the introduction on the market of plastic materials of completely new compositions and endowed with a very great resistance to water, brought us to believe that it was, henceforth, possible to enlarge the field of our investigations by pushing our studies as far as the maximum temperature of 95° C that water permits us to obtain and also to make a comparative study by measuring separately the permeability of our plastic materials to water in the liquid state as well as to water in the form of steam.

-Page Four-

To our knowledge, this was the first time that, thanks to the hygrophotographic technique, such a program of studies was made possible.

The experiments at normal temperature were carried out by plunging a part of our preparations into liquid water contained in a dessiccator and placing the other part on a support placed above in the atmosphere saturated by steam which covers the liquid.

For higher temperatures, we were obliged to operate separately for the water and the vapor heated at the same temperature, for the vapor is never at the same temperature as the liquid which it covers.

We had difficulties in the preparation of bags by means of Tedlar and Saran films with which it was impossible for us to obtain a vacuum by soldering with a flame. By consequence, the experiments were carried out at the normal atmospheric pressure. However, the Saran film which we had this time was very different from the sample previously used.

For the plastics which are sufficiently permeable to water, we have noticed not too great differences between the permeability to water and to steam in the zone of weak temperatures, differences which became less and less sensitive in proportion as we increased this temperature. The ~~two~~ permeabilities became practically equal

-Page Five-

at the temperatures of 85 and of 95° C (Tedlar and Profax); except for the Saran whose permeability to steam in this same zone of temperatures is clearly revealed less elevated than the permeability to water, without doubt because of the profound modification undergone by the film at the contact of hot water. In the case of FEP, the differences of the two values remained constant, while for the plastic materials excessively little permeable to water, as the Kel-F, no difference was verified, their permeability to water being the same as their permeability to water vapor for all the temperatures studied.

INTRODUCTION

This is a final report summarising the results obtained during the period February 1, 1962 through January 31, 1963, on the project to determine the permeability of packaging materials to water and moisture by the hygrophotographic method.

This research, carried out under Contract Number DA-91-591-EUC-2152 is the continuation of the work carried out under Contract Number DA-91-591-EUC-1704 and 1394.

METHODS AND PROCEDURE

The materials studied included: Films

Kel-F Shamban	143	μ
Kel-F Shamban	55	μ
Kel-F 82	157	μ
Kel-F 81	155	μ
Profax	79	μ
FEP	45	μ
Saran	47	μ
Tedlar	102	μ
Manolène	300	μ
d°	200	μ
d°	150	μ
d°	100	μ
d°	50	μ
d°	30	μ

In the present investigation, we have definitely adopted artificial light for the blackening of hygro-photographic plates before their calibration, which constitutes a step nearer the standardization of the method. The plates, being always of the same nature, constantly receive the same quantity of light.

The hygrophotographic plates, always manufactured by transformation of a same mark of commercial photographic plates (Guilleminot Lactate plates, containing no coloring) are placed at a fixed distance from a fluorescent light called "daylight".

The plates are exposed to this light during a limited time, that is to say two hours, permitting the establishment once and for all, of the duration of the calibration to 12 minutes. The setting time necessary for the final printing on "Guilleminot Collodium" plates is also about the same and is equal to about 9 seconds.

The Tedlar film having replaced the Teslar film which we have previously studied, was clearly thicker than the samples of Teslar. It is, however, better composed than the Teslar at the moment of the manufacturing of the bags, but once again we were unable to create a vacuum in the bags obtained in this way. By consequence, we have studied the permeability of Tedlar at atmospheric pressure.

The Saran film which we have had this time, is completely different from that which we have previously had. The present film is very supple and elastic and is without doubt highly plasticized, in a way in which it was impossible for us to obtain a solder by flame. We were, therefore, obliged to achieve the solder with a pressing iron and to study the permeability at atmospheric pressure, as for the Tedlar film. When, after having created a vacuum, we had wanted to solder the Tedlar or Saran film by the flame of a Bunsen burner, it contracted, became deformed and pierced.

We have also studied the permeability of different samples of Kel-F received from the Minnesota Mining and Manufacturing Co or prepared by the Shamban Co., Culver City, California. These films present no difficulty and are successfully worked with for the manufacturing of bags by solder by the aid of a pressing iron for the creation of a vacuum and for the sealing, afterwards, by a flame in front of a hypodermic needle, serving to create the vacuum.

The Shamban 66 μ film, heated at 95° C, undergoes without doubt, a dilatation and afterwards a sudden contraction when taken out of hot water as we detected the immediate formation of multiple creases in parallel lines.

The Profax or polypropylene as well as the Manolène or polyethylene films, which are very easy to handle, permitted us to manufacture bags with the small flame of a Bunsen burner which serve equally for sealing the bags after the creation of a vacuum.

One more remark relative to the behavior of hygro-photographic plates at high temperatures.

We have noticed that when we heated our plates enveloped in films at temperatures of 85 and especially of 95° C, these plates underwent a certain browning recognizable especially on the examination of the side of the support, which, in its normal state, should be a light yellow. We must remember that this condition is absolutely necessary for the calibration and, in order to keep this purity of this yellow color on the back of the plates, we achieve the irradiation before usage by protecting the support side, that is to say, by placing the plates in a photographic pressing frame and irradiating them in this way placed in their frame.

The browning of the plates during heating highly diminishes their transparency and the results of the measures are no longer acceptable. Fortunately, this change is not produced throughout the totality of the sensitive surface and it is still possible to achieve

valid measures at the points remaining intact. Sometimes, this browning does not exist at all, in a way in which when such a change is produced, it is necessary to begin the tests once again in order to be able to choose the best results.

We have carried out many tests to find out the reasons for the partial opacification of hygrophotographic plates at high temperatures. The unblackened 9 x 12 cm hygrophotographic plate having been divided into four parts, the first is enveloped in 200 μ Manolène, the second in Kel-F 143 μ . these two samples were then heated in water at 80° C, the fourth piece of plate was conserved in a box without any treatment and the third piece was heated in a dry oven without a plastic sheet, at the same temperature; after 20 minutes of heating, we have reassembled the different pieces and have photographed them, noticing no change due to the action of the heat.

We have then blackened two plates, numbered 1 and 2, which we have divided into 6 parts each. Next, we have enveloped two pieces of plate N° 1 in a Manolene 100 μ bag. In a second bag, we have placed two pieces of plate N° 2, without having submitted them to dessiccation in a dessicator on P_2O_5 and we have heated them in water at 85° C. After a half an hour of heating, we have photogra-

phed them. They were normally discolored without having undergone opacification. We have put the remainder of these two plates in the dessicator on P_2O_5 and, six hours later, we have once again taken two pieces of each of the two plates and have enveloped them in two Manolène 100 μ bags, then heated as before in water at $85^\circ C$ during a half an hour. On photographing them, we have seen that plate N° 2 had undergone an important opacification, while plate N° 1 remained in a normal state. The last pieces of these plates were conserved again in the dessicator during eight days and were then treated as previously. This time the two plates had undergone an opacification sensitively more important than the previous time. Opacification is also sensitive sometimes after 12 hours of conservation and of dehydration on P_2O_5 . In conclusion, it seems to us, therefore, that this opacification by heating at a high temperature is due to the long conservation of the plates on P_2O_5 and to their extreme and prolonged dehydration which is the result.

TABLE I

Action of the temperature on the permeability of various
plastic sheets

P $\mu\text{g}.\text{mm}/\text{mm}^2/\text{h} \cdot 10^{-3}$ 25° 35° 45° 55° 65° 75° 85° 95°

Kel-F 143 μ

in the water

1.5 6.8 9.6 586 1000 3208 5068 8236

in the water vapor

1.4 6.2 10 580 985 3159 5008 8200

Kel-F 55 μ

in the water

0.5 3.3 8.6 270 500 1056 1182 1501

in the water vapor

none

Kel-F 82 157 μ

in the water

1.5 30 187 549 785

in the water vapor

1.5 29 172 518 760

Kel-F 81 155 μ

in the water

1.5

in the water vapor

1.5

Profax 79 μ

in the water

8.7 20 147 487 587 711 2528 3555

in the water vapor

6.8 17 101 527 661 916 2489 3500

TABLE I (continued from p.12)

P $\mu\text{g}.\text{mm}/\text{mm}^2/\text{h} \cdot 10^{13}$	25°	35°	45°	55°	65°	75°	85°	95°
FEP 45 μ	in the water							
	1.3	72	180	207	322	794	2457	4254
	in the water vapor							
	0.7	21	144	197	295	750	2357	4200
Saran 47 μ	in the water							
	2.3	80	220	518	887	1262	5078	6204
	in the water vapor							
	0.9	78	206	318	857	1141	4976	5041
Tedlar 102 μ	in the water							
	11	95	260	999	2213	4376	9118	13756
	in the water vapor							
	9	87	206	977	1469	2249	8404	13345
Manolène 300 μ	in the water							
	3	26	150	318	618	1830	2460	2645
	in the water vapor							
	3	24	147	317	618	1830	2459	2640
Manolène 200 μ	in the water							
	2	20	145	324	621	1840	2480	2655
	in the water vapor							
	2	19	144	320	619	1835	2474	2650
Manolène 150 μ	in the water							
	3.5	35	165	334	644	1904	2485	2679
	in the water vapor							
	3.5	34	165	333	641	1900	2481	2675

TABLE I (continued from p.13)

P $\mu\text{g}.\text{mm}/\text{mm}^2/\text{h} \cdot 10^{-3}$	25°	35°	45°	55°	65°	75°	85°	95°
Manolène 100 μ	in the water							
	4.5	39	211	416	781	1720	2960	3439
	in the water vapor							
	4.3	34	203	411	778	1715	2960	3439
Manolène 50 μ	in the water							
	5.5	37	210	421	783	1735	2970	3460
	in the water vapor							
	5.1	35	208	420	780	1729	2965	3655
Manolène 30 μ	in the water							
	6.1	45	245	431	790	1753	3006	3945
	in the water vapor							
	6.0	43	237	429	785	1747	3001	3938
Manolène 20 μ	in the water							
	8.1	50	306	486	825	1866	3081	4060
	in the water vapor							
	7.8	46	300	484	823	1858	3078	4059

DISCUSSION OF RESULTS

Generally speaking, the comparative study of the permeability to water on the one hand and to water vapor on the other, for the same given temperature, showed that this permeability is slightly higher in the case of water than in the case of water vapor at low temperatures when it concerns relatively permeable plastic materials as Tedlar or Profax. At high temperatures (85 and 95° C), they become practically equal. In all evidence, the permeability of polypropylene is clearly weaker than that of Tedlar.

In the case of FEP, of which the permeability to water is also a little higher than the permeability to steam, the deviation of the two values remains sensitively the same for all the scale of temperatures, while it is accentuated for Saran.

As for Kel-F, we have studied several samples, the Kel-F 55 and 143 μ of the Kel-F Shamban Co and the Kel-F 81 and 82 of Minnesota Mining and Manufacturing Co. Unfortunately, the samples of Kel-F 81 and 82 at our disposal being clearly insufficient, enabled us to make but a partial study of the later.

In spite of the incomplete character of our studies of Kel-F 81 and 82, the comparison of the results obtained with the three sorts of Kel-F permitted us to con-

-Page Sixteen-

clude that their permeability, at normal temperature, is about the same, for water as well as for steam.

We had noticed a similar fact in studying the permeability of paraffine wax to water. The discoloration of the plates enveloped in paraffine and placed in water or in a box, submitted only to the influence of atmospheric humidity at normal temperature, took place in the same manner and in an identical delay, which we have explained on taking account of the very weak value of the coefficient of solubility of water in paraffine wax (J. Sivadjian, Journ de Chimie Physique, 1959, 56, 372).

On the other hand, the new Manolene seems to have greatly improved its properties, since for the Manolene 200 μ , for example, the permeability to water of 5.25 (Final technical Report N° 1, January 1961, p.14) diminished and became $2 \mu\text{g}/\text{mm}/\text{mm}^2/\text{h}$.

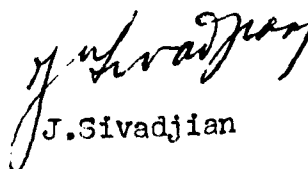
ANNEX

This research was accomplished under the direction of the principal investigator, M. Joseph Sivadjian, and the actual work carried out by Mr. David Ribeiro, whose knowledge in this domain as well as his great capability were of much assistance in the achievement of this work. Miss Jeannine Sivadjian was of efficient assistance in the technical part of this work and in the preparation of our reports.

This research demanded more than 400 experiments and densitometric measures and required 2112 hours of work.

The cost of the material used was approximately 400 dollars.

The Principal Investigator


J. Sivadjian